Enhanced Reactivity of Lithium and Copper at High Pressure

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Abstract

High pressure can profoundly affect electronic structure and reactivity, creating compounds between elements that do not react at ambient conditions. Lithium is known to react with gold and silver, however no copper compounds are known to date. By compressing mixtures of the elements in diamond-anvil cells, compounds of lithium and copper have been synthesized and unambiguously characterized by X-ray diffraction for the first time. Pressures as low as 1 GPa lead to the formation of a complex layered phase LiCu, displaying two-dimensional kagomé lattice layers of Cu atoms. Above 5 GPa, the layered Cu-Cu bonding is replaced by linear chains of Cu atoms in the high-pressure phase Li_2Cu. This phase is stable to 25 GPa, the highest pressure reached in this study.

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At atmospheric pressure, binary compounds of lithium (Li) and the noble metals gold (Au) and silver (Ag) have been known for some time. Detailed exploration of the composition-temperature phase diagrams have revealed a wealth of different structures and compositions ranging from simple, cubic phases such as LiAg,[1,2] Li_3Au,[3] and $LiAu_3$[3] to highly complex 'gamma-brass' structures in compounds such as Li_9Ag_4[4] and $Li_{15}Au_4$, which contains more than 75 atoms in the unit cell.[3]

Given the wealth of structural variety it is perhaps surprising that Li and copper (Cu) are reportedly unreactive, forming no known compounds. Early work by Pastorello[5] and then Klemm[6] found no evidence of Li-Cu compounds and the most recent thermodynamic measurements posit the existence of an intermetallic Li_3Cu_2 phase at temperatures between 753 and 923 K.[7] First-principles calculations suggests only one compound should exist, LiCu, again stable at high temperatures.[8]

The use of high-pressure reaction conditions is a widely exploited technique to synthesize novel compounds with unusual physical and chemical properties.[9–11] The reactivity of Li under pressure has to date been limited to computational studies using structure-searching methods. A number of Li-compounds have been predicted to form at high pressures with Be,[12] Au,[13] Zn,[14] and Fe,[15] making this a promising approach to modulate the reactivity of the Li-Cu system. It should also be noted that because of the reported inertness, Cu has been widely used as an electrodes for conductivity measurements of Li under pressure, however the possibility of reaction between the two species has not been explored.[16–18]

Herein we show that the application of modest pressures *i.e.* < 1 GPa (10000 atmospheres), causes the reaction of Li and Cu forming previously unknown compounds at room temperature. The structures of these phases have been determined by high-pressure X-ray diffraction. At low pressures we observe a complex phase, with stoichiometry LiCu, consisting of layers of Cu atoms arranged in a kagomé lattice. Above 5 GPa, the Cu-Cu bonding changes drastically: transitioning from 2D layers to linear chains of Cu atoms observed in the high-pressure Li_2Cu phase. This phase is stable to 25 GPa, the highest pressure reached

in this study.

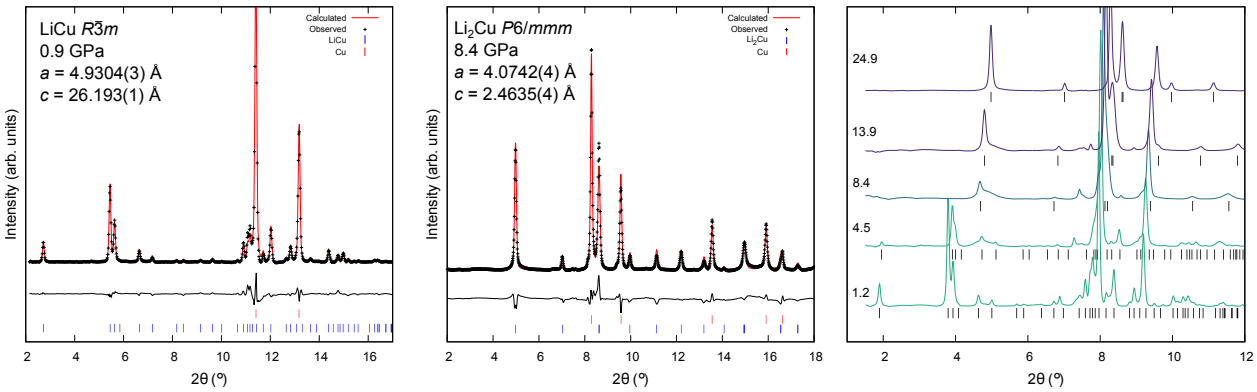

Figure 1: X-ray diffraction patterns collected at (a) 0.9 GPa ($\lambda = 0.4136$ Å) showing the numerous peaks corresponding to the low-pressure phase $Li_{19.5}Cu_{19.5}$. Tick marks indicate the location of Bragg peaks from $Li_{19.5}Cu_{19.5}$, Cu, and Li; (b) X-ray diffraction pattern ($\lambda = 0.2889$ Å) collected at 24.9 GPa. All peaks can be indexed to a hexagonal high-pressure compound, Li_2Cu crystallizing in $P6/mmm$ which remains stable to at least 24.9 GPa; (c) X-ray diffraction patterns ($\lambda = 0.2889$ Å) showing the transition from LiCu to Li_2Cu. Tick marks indicate peaks from Li-Cu compounds, unmarked peaks are due to Cu and Li, pressures (GPa) are given in corresponding labels.

During loading of the DACs, grains of Cu powder were placed directly on the surface of the Li metal with no visible reaction occurring. After sealing the sample in the DAC gasket chamber whilst in an inert atmosphere, the Cu powder lost its characteristic colour leaving grey, textured regions on the surface of the sample.

Attempts were made to keep the initial pressure as low as possible while also maintaining a hermetic seal on the sample chamber, the lowest pressure achieved was 0.9(1) GPa. X-ray diffraction data at this pressure is shown in Figure 1 and is highly complex, containing peaks due to unreacted Cu and Li indicating the system did not fully reach equilibrium. However, all remaining peaks can indexed to a rhombohedral unit cell, $a = 4.9304(3)$ Å, $c = 26.193(1)$ Å at 1.25 GPa. Diffraction patterns for this phase were typically highly 'spotty' leading to unreliable integrated intensities, although unit-cell dimensions could be extracted. However, one run produced powder diffraction rings of sufficient quality to allow Rietveld full profile refinement. Solution of the structure reveals a new 'μ-phase' intermetallic with stoichiometry $Li_{19.5}Cu_{19.5}$, (in Pearson notation: LiCu-$R39$). Two Cu atom sites were readily identified at

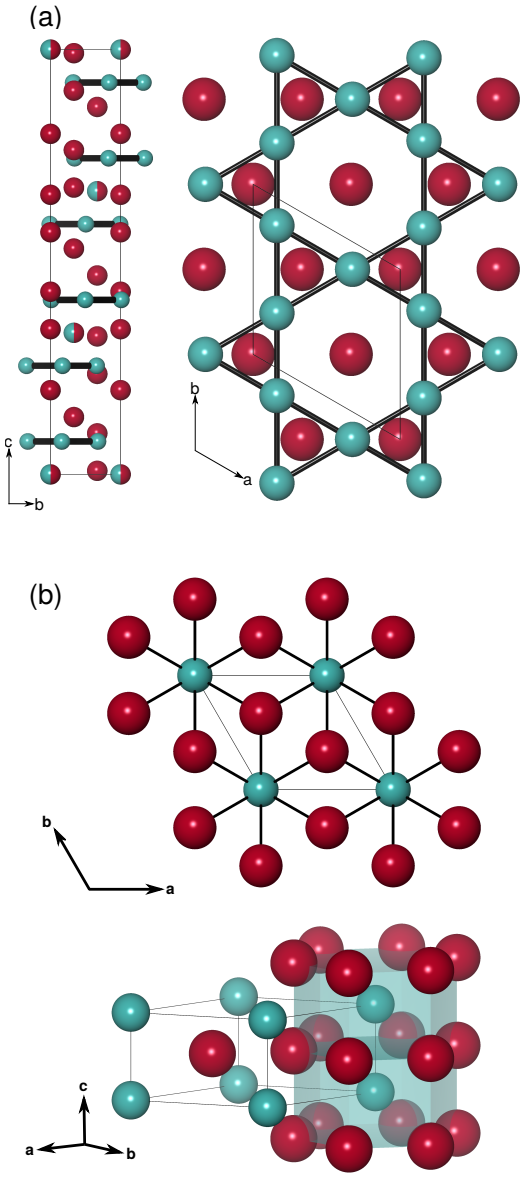

Figure 2: (a) Crystal structure of LiCu-$R39$ showing the copper kagomé lattices stacked along the c axis. Right panel shows a single lattice layer; (b) the structure of Li_2Cu consists of $Li_{12}Cu$ hexagonal prisms stacked along the c axis. Lithium atoms shown in red, copper atoms shown in blue.

the $18h$ and $3a$ sites, one fully ordered ($18h$) and one half-occupied ($3a$). Three Li-atom sites were located in difference Fourier maps, the fourth half-occupied site is shared with Cu (Figure 2).

Table 1: Atomic position parameters for LiCu-$R39$ at 0.9 GPa.

Atom	Site	x	y	z
Cu1	$18h$	0.3240(10)	0.1620(5)	0.07758(11)
Cu2	$3a$	0	0	0
Li1	$6c$	2/3	1/3	0.13499
Li2	$6c$	1/3	2/3	0.09667
Li3	$6c$	1/3	2/3	0.00850
Li4	$3a$	0	0	0

The stoichiometry of this phase was determined by refining the occupancy of the disordered Cu-atom site and this is in agreement with volume *vs.* pressure relationships for the LiCu-$R39$ phase compared to hypothetical volumes for Li-Cu alloys obeying Vergard's law with formulae $Li_{19.5}Cu_{19.5}$ (see Figure 3(a) and insert). Due to the low scattering factor for Li, the Li atomic coordinates for this phase could not be stably refined, however the locations as determined from Fourier difference maps are reported in Table 1 and are in general agreement with those found for analogous μ-phase structures. The final agreement factors for refinement against the data at 0.9 GPa are $wR_p = 0.022$ and $R_p = 0.013$ (Fig. 1(a)).

μ-phase intermetallics have been found in at least twelve binary A-B systems where A and B are both transition metals, A from row 4 or 5 and B from row 3.[19–21] These phases can show a range of stoichiometries with $\%A$ varying between 40% to 55% depending upon the identities of A and B.[21] To our knowledge this is the first known example of a μ-phase intermetallic structure formed by an alkali metal.

LiCu has a layered structure, each unit cell contains six layers of Cu atoms arranged in two symmetry-independent kagomé lattices with Cu-Cu distances of 2.381(12) and 2.550(12) Å at 1.25 GPa. These Cu-Cu bonds are shorter than those in bulk Cu at the same pressure, reflecting the reduced dimensionality of the Cu-Cu bonding (Figure 4). This strong Cu-Cu bonding results in highly anisotropic compressibility, with linear modulii for the two axes

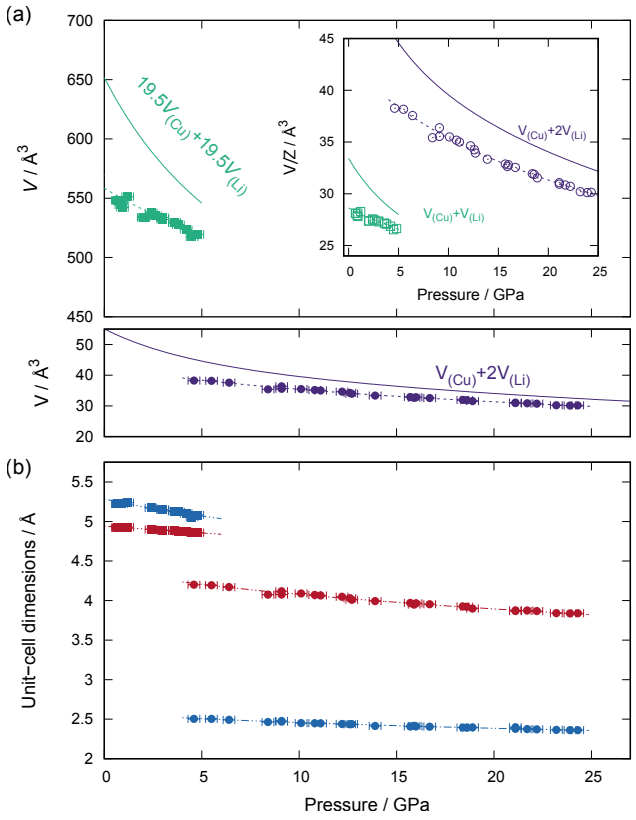

Figure 3: (a) Changes in unit-cell volumes and volume-per-formula unit (V/Z) with pressure for Li-Cu compounds. Fitted equations-of-state are shown with dashed lines, calculated volumes derived from atomic equations of state shown with solid lines of corresponding colour; (b) Changes in unit-cell dimensions a (red) and c (blue) for LiCu (squares) and Li_2Cu (circles). Linear moduli shown with dashed lines. $c_{(LiCu)}$ is divided by 5 for clarity.

being 282(76) and 93(10) GPa for a and c, respectively. Unit-cell dimensions are shown in Figure 3(b).

LiCu is stable to 4.75 GPa above which peaks corresponding to this phase began to disappear to be replaced by a smaller number of peaks corresponding to a new high-pressure phase and accompanied by a broad band of diffuse scattering centered on the (104) reflection (see Fig. 1(c)). By 8.4 GPa the transformation was complete. Again, X-ray diffraction patterns contained peaks corresponding to unreacted Cu and Li. The additional lines could be readily indexed to a hexagonal cell with unit-cell dimensions (at 8.4 GPa): $a = 4.0742(4)$ Å, $c = 2.4635(4)$ Å.

Structure solution by charge flipping[22] and subsequent Rietveld analysis shows the phase to have composition Li_2Cu, space group $P6/mmm$ ($CaHg_2$-type), analogous to Li_2Pt.[23] The final agreement factors for refinement against the data at 24.9 GPa are $wR_p = 0.015$ and $R_p = 0.007$ (Fig. 1(b)). In this phase, Cu atoms (at 0, 0, 0 1a) are arranged in chains along the c-axis, each chain passes perpendicular through stacks of Li atoms (at 1/3, 2/3, 1/2, 2d) arranged hexagonally forming graphene-like sheets (Figure 2). Each Cu atom is coordinated by 12 Li atoms and 2 Cu atoms forming stacked hexagonal prisms. On decompression Li_2Cu remains stable to 4.6 GPa, below which peaks due to this phase disappear to be fully replaced by those of LiCu-$R39$ by 2.6 GPa.

In LiCu there are three symmetry-independent Cu-Cu nearest-neighbour distances: two within the kagomé layers and one to the disordered Cu site between these layers. Under compression, Cu-Cu distances within one of the two layers increases (+0.12(2) Å) under pressure while reducing (−0.17(2) Å) in the other. Upon transition to Li_2Cu, Cu atoms form chains with only one nearest neighbour (distance give by unit-cell length c) which is only marginally shorter than the interatomic distance in pure Cu at the same pressure, shown by the solid line in Figure 4. The same holds true for interlayer distances in LiCu (next-nearest neighbours) which, despite the significant scatter in these values, clearly resolve to one upon transitioning to Li_2Cu, corresponding to the a unit-cell length.

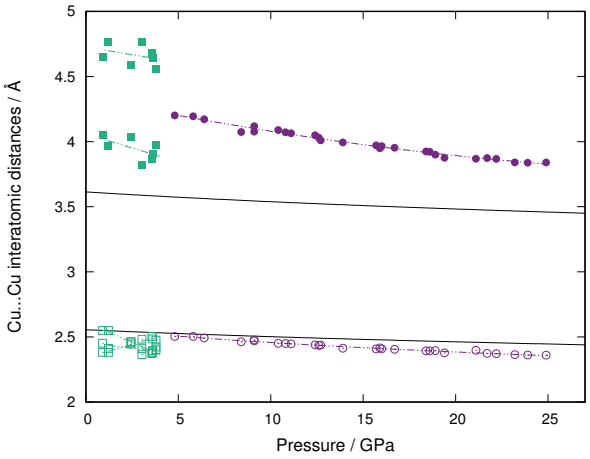

Figure 4: Changes in Cu...Cu interatomic distances with pressure for LiCu (green squares) and Li_2Cu (purple circles). Nearest-neighbour distances are shown with open symbols, next-nearest-neighbour distances with filled symbols. Corresponding distances in elemental Cu shown with solid lines, dashed lines are guides to the eye.

The spontaneous formation of Li-Cu compounds under such modest pressures suggests that studies investigating the electrical properties of Li using Cu electrodes would have contained significant contamination due to these reactions.[16–18]

Compounds adopting the $P6/mmm$ structure of Li_2Pt[23] (amongst other $CaHg_2$-type compounds) have been proposed to exhibit possible Dirac semimetal behaviour as a result of linear chains of atoms ordered hexagonally in two dimensions.[24] In calculations, spin-orbit coupling leads to the 'gapping-out' of the Dirac semimetal state in Li_2Pt however,the strength of spin-orbit coupling is dependent on the atomic number of the atoms forming the chains and scales Z^4. The combination of weaker spin-orbit coupling and the large stable pressure range in which interatomic distances can be tuned (at least 20 GPa) makes Li_2Cu an intriguing candidate material for this phenomenon.

In conclusion, the application of modest pressures *i.e.* < 1 GPa leads to the formation of the first unambiguously characterised Li-Cu compounds. At low pressures we observe the formation of LiCu-$R39$ adopting a remarkably complex layered structure with Cu atoms arranged in kagomé lattices. Above 5 GPa, LiCu-$R39$ is transformed to a new high-pressure phase Li_2Cu which is stable to at least 25 GPa. This transition is marked by the reduction of

Cu-Cu bonding from two-dimensional layers to one-dimensional chains. Our findings show the power of applying high pressure as an effective method for materials discovery.

All samples were made by the direct combination of Li and Cu loaded into diamond-anvil cells (DACs). All loadings were carried out in an argon-atmosphere glovebox. Elemental Li (Alfa Aesar 99.9%) was first packed into the sample chamber formed by a rhenium gasket. Grains of Cu (Alfa Aesar 99.9%) were placed on the surface of the packed Li and the cell was closed. The concentration of copper was controlled by visual estimation during loading. Lithium presents a challenge for high-pressure experiments at room temperature, as above pressures of 25 GPa, Li reacts and diffuses into the diamond anvils causing embrittlement and subsequent failure.[25] As such, we limited our study to pressures below 25 GPa at room temperature.

Angle-dispersive X-ray diffraction patterns were recorded on PerkinElmer XRD21 and Marr345 image-plate detectors with synchrotron radiation sources with energies in the range 30-42 keV. Two-dimensional image-plate data were integrated with DIOPTAS[26] to yield intensity *vs.* 2θ plots. Patterns were indexed with GSAS-II,[27] Le Bail[28] and Rietveld[29] refinements were carried out in JANA2006.[30]

Pressure was determined with reference to the literature equation-of-state data for the elements Li,[25] and Cu.[31] Volume- and linear-equation of state parameters were determined using EOSFIT 7.[32]

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